

2. Remarks

Claim Wording

All of the claims recite the wording used in the specification as modified by amendment filed on June 27, 2003 to describe aerosol pyrolysis reactant solutions as solutions comprising one or more dissolved metals and/or metal-containing compounds.

Claim Rejections – 35 USC § 102

Claims 25, 28-33, 38, 39, 46 and 47 were rejected under 35 U.S.C. 102(b) as being anticipated by Douglas et al (US 4,023,961). Claims 28, 29, 31, 32, 46 and 47 have been canceled, and no corollary replacement claims have been submitted. Claims 25, 29, 30, 33, 38 and 39 have been replaced by new claims 51, 53, 54, 55, 59 and 60, respectively. All of the new claims recite the present invention as being of particular use in the field of thin-film photovoltaics. The applicants respectfully submit that claims 51, 53, 54, 55, 59 and 60 are patentable over Douglas et al.

Claims 25 and 29 have been replaced with claims 51 and 53. Claims 51 and 53 relate to single-phase, mixed-metal, metal oxide particulate materials. The present invention teaches new art on how to prepare single-phase oxide materials comprising Cu plus In and/or Ga. For example, Example 1 of the present invention teaches the preparation of single-phase $\text{Cu}_2\text{In}_2\text{O}_5$.

In the case of mixed-metal materials comprising oxygen, Douglas et al teach the formation of multi-phase materials comprising multiple metal oxides in a metal oxide / metal oxide composite (column 2, lines 9-10 and 28-31). Multinary composite materials comprising a metal oxide prepared according to Douglas et al have multiple phases (column 7, lines 11-17). The methods of Douglas et al do not result in single-phase, mixed-metal, oxide materials. For example, Douglas et al disclose that solutions comprising Cu and Cd and solutions comprising Cu and Zn produce multi-phase CuO/CdO and CuO/ZnO , respectively (column 9, lines 15-38). One skilled in the art would expect from the teachings of Douglas et al that solutions comprising Cu and In, Cu and Ga, or Cu, In and Ga would similarly produce multi-phase $\text{CuO/In}_2\text{O}_3$, $\text{CuO/Ga}_2\text{O}_3$, and $\text{CuO/In}_2\text{O}_3/\text{Ga}_2\text{O}_3$, respectively, when droplets of said solutions are reacted in an oxidizing atmosphere. The present invention teaches the unexpected result that Cu, In and Ga form single-phase oxide particles when droplets of reactant solutions are heated in an oxidizing atmosphere.

The Final Office Action of July 2003 on page 4 in the first full paragraph states the position that, in light of the teachings of the present invention, a solution of silver and cadmium nitrates processed in a flame or hot air at 550°C would yield a single-phase powder; however, Douglas et al contradict this position, referring to the resulting composite powder as a silver-metal oxide powder (column 9, line 64), i.e. a multi-phase material comprising silver metal and cadmium oxide. The fact that Douglas et al report multi-phase metal / metal oxide materials under preparation conditions similar to those that the present invention teaches can be used to form single-phase materials underscores the significant differences in the chemistries of the specific noble metals disclosed by Douglas et al (Ag,

Au, Pt and Pd) and the specific metals (i.e. Cu, In and Ga) and processing conditions (i.e. atmospheres) disclosed in the present invention.

Given that claims 51 and 53 disclose a method for preparing single-phase, mixed-metal, metal oxide particulate materials and that Douglas et al teach that their method of preparing mixed-metal materials comprising a metal oxide leads invariably to multi-phase materials, the applicants respectfully submit that Douglas et al teach away from the present invention and that claims 51 and 53 are patentable over the cited art and should be allowed.

Claims 30 and 33 have been replaced with new claims 54 and 55. Claims 54 and 55 relate to the preparation of mixed-metal particles comprising Cu in a metallic phase and In and/or Ga in an oxide phase by heating droplets of a solution comprising dissolved Cu and In and/or Ga in a reducing atmosphere. For example, Example 3 of the present invention discloses the preparation of multi-phase, mixed-metal particles comprising copper metal and indium oxide by heating droplets at about 500°C in an atmosphere comprising about 10 vol% hydrogen.

Douglas et al teach that for specific noble metals (i.e. Ag, Au, Pt and Pd [see column 2, lines 20-22]) one can use aerosol pyrolysis in an oxidizing atmosphere to prepare particles comprising a metallic phase by thermal decomposition via a gas flame, hot air or other heating methods (column 9, lines 53-62). All of the examples disclosed by Douglas et al of materials comprising a metallic phase involve one or more of the four listed noble metals, and all of the methods disclosed by Douglas et al in which these noble metals are used result in materials comprising a metallic phase under all processing conditions taught by Douglas et al. This stands in sharp contrast to the teachings of the present invention in which a solution comprising, for example, Cu and In can be made to yield a single-phase multinary oxide material (i.e. $\text{Cu}_2\text{In}_2\text{O}_5$), a multi-phase material comprising multiple oxides (e.g. $\text{CuO-In}_2\text{O}_3$), or a multi-phase material comprising a non-oxide phase (e.g. $\text{Cu-In}_2\text{O}_3$) depending on the atmosphere in which droplets are heated. The key differences are the chemistry of the specific metals and the use in the present invention of specific heating atmospheres to obtain unique particle characteristics.

The differences between the materials taught by Douglas et al and those taught in the present invention are evident in the scientific literature. Douglas et al teach that a metallic phase can be achieved in air using noble metals. Noble metals are very resistant to oxidation whereas base metals such as copper readily oxidize when heated in air. For example, copper forms pink Cu_2O in air below 100°C and rapidly forms black CuO in air above 300°C. Reactant solutions comprising Cu, In and Ga would be expected to form oxides when heated appreciably in oxidizing conditions. For example, indium nitrate pyrolyzed in air at 400°C forms In_2O_3 (see H. Schroeder in *Optica Acta*, July 1962, vol 9, pages 249-254); and a solution of indium and copper nitrates spray pyrolyzed in air at 150°C forms a copper indium oxide film (M. Beck and M. Cocivera, *Thin Solid Films* 272 (1996) 71-82). In contrast, oxides of Au spontaneously decompose to metallic Au at room temperature, and Pt is sufficiently resistant to oxidation that it can be used as a crucible in air at 1000°C to prepare ceramics (L. Kassab et al., *Optics Express* 6 (2000) p. 104). The particular differences between copper and silver are evident in, for example, the use by Xu et al of thin silver coatings to mitigate the deleterious susceptibility of copper powder to oxidation (X. Xu et al, *Materials Letters* 57 (2003) 3987-3991).

The teachings of Douglas et al vis-à-vis particles comprising a metallic phase are limited in their utility to specific noble metals. One skilled in the art attempting to directly apply the teachings of Douglas et al to Cu, In and Ga would not produce materials comprising a metallic phase, rather one would produce only oxide phases. The unique teachings of the present invention are needed with the claimed metals to prepare materials with the specific advantageous properties, i.e. submicron particles comprising Cu in a metallic phase and In and/or Ga in an oxide phase.

Even with a combination of the teachings of Douglas et al vis-à-vis using aerosol pyrolysis to form metal oxides and the teachings of others that certain oxides can be reduced to metals by annealing in reducing atmospheres, given the phase relationships of Cu, In, Ga and O, one skilled in the art would not have anticipated producing heterogeneous materials with significant phase segregation into Cu metal and In, Ga oxide phases. Under highly reducing conditions one might expect to reduce all of the oxides to metals; but then one would anticipate compositional changes due to differential vaporization, and particles would not retain an oxide phase useful for mitigating macroscopic phase segregation during subsequent processing of layers of particles for solar cells. At less reducing conditions, one might hope to achieve differential reduction rates of various oxides, but it is unexpected that copper can be fully reduced to a metallic phase while indium and/or gallium remain in an oxide phase.

Given that claims 54 and 55 relate to specific metals that are in their nature quite different from the metals disclosed by Douglas et al and that these differences in metal natures yield sharply different results when processed by the teachings of Douglas et al and the teachings of the present invention, the applicants respectfully submit that Douglas et al teach away from the present invention and that claims 54 and 55 are patentable over the cited art and should be allowed.

Claims 38 and 39 have been replaced by new claims 59 and 60. Claims 59 and 60 relate to the preparation of mixed-metal particles comprising multiple oxide phases by preparing a reactant solution comprising Cu and In and/or Ga, and heating droplets of the solution in a substantially inert atmosphere or in a reducing atmosphere. The present invention teaches that proper selection of the heating atmosphere is essential in producing specific advantageous particle characteristics. For example, Examples 1-3 of the present invention disclose that identical reactant solutions can be made to yield single-phase oxides, multi-phase oxides or multi-phase metal / oxide composites with the proper selection of heating atmospheres.

Douglas et al teach forming mixed-metal oxide particles by thermal decomposition of droplets in oxidizing atmospheres such as in a gas flame (column 2, lines 57-59) or hot air (column 9, lines 59-60). In all cases where the reactant solutions of Douglas et al comprise base metals such as copper (column 2, lines 22-25) the resulting particles comprise those metals in separate single-metal oxide phases (see for example column 9, lines 15-38 where CuO/CdO and CuO/ZnO composite materials are disclosed). Douglas et al teach away from the present invention by disclosing that heating in an oxidizing environment of droplets of mixed-metal reactant solutions comprising base metals produce oxide / oxide materials. One skilled in the art seeking to produce multi-phase particles comprising Cu plus In and/or Ga would be led by the teachings of Douglas et al to the false conclusion

that heating droplets of a solution containing Cu plus In and/or Ga would produce multi-phase particles when heated in an oxidizing atmosphere, where as taught by the present invention the production of multi-phase particles from such solutions requires that droplets be heated in a substantially inert atmosphere or a reducing atmosphere.

Given that claims 59 and 60 teach the advantages of using certain processing atmospheres to achieve specific particle characteristics when producing particles comprising certain metals and that the disclosures of Douglas et al teach away from the processing avenues of the present invention, the applicants respectfully submit that Douglas et al teach away from the present invention and that claims 59 and 60 are patentable over the cited art and should be allowed.

The new art disclosed by the present invention is patentably distinct from Douglas et al and would not be obvious to one skilled in the art. Accordingly, applicants respectfully submit that the claims as amended are patentable over the cited art and should be allowed.

Claim Rejections – 35 USC § 103

Claims 26, 34, 36, 37, 40, 42-45 and 48-50 were rejected under 35 U.S.C. 103(a) as being unpatentable over Douglas et al in view of Ranade et al (US 5,928,405). Claims 26, 34, 40, 42, and 44-50 have been canceled, and no corollary replacement claims have been submitted. Claims 36, 37 and 43 have been replaced by new claims 57, 58 and 61, respectively. The applicants will swear behind Ranade et al. Accordingly, the applications respectfully submit that claims 57, 58 and 61 are patentable over Douglas et al in view of Ranade et al.

Claims 26, 34, 36, 37, 40, 42, 48 and 50 were rejected under 35 U.S.C. 103(a) as being unpatentable over Douglas et al in view of Schmidberger et al (US 4,396,420). Claims 26, 34, 40, 42, 48 and 50 have been canceled, and no corollary replacement claims have been submitted. Claims 36 and 37 have been replaced by new claims 57 and 58. The applicants respectfully submit that claims 57 and 58 are patentable over Douglas et al in view of Schmidberger et al.

Schmidberger et al teach a method for making Ag / metal oxide particles with diameters in the range of 1 – 10 microns (see column 2, lines 44-46) wherein the particles have individual metal oxide grains with dimensions of less than 1 micron (see column 2, lines 46-47). Schmidberger et al makes a clear distinction between the size of the composite particles and the size of the metal oxide precipitate grains. The present invention teaches advantages related to average diameters of less than about 1 micron for specific particles, not particles' constituent grains.

The new art disclosed by the present invention is patentably distinct from Schmidberger et al in light of Douglas and would not be obvious to one skilled in the art. Accordingly, applicants respectfully submit that the new claims 57 and 58 are patentable over the cited art and should be allowed.

Claims 27, 35 and 41 were rejected under 35 U.S.C. 103(a) as being unpatentable over Douglas et al in view of Yamada et al (US 4,173,518). Claim 41 has been canceled, and no corollary replacement claims have been submitted. Claims 27 and 35 have been replaced by new claims 52 and 56. The applicants respectfully submit that claims 52 and 56 are patentable over Douglas et al in view of Yamada et al.

Yamada et al teach the use of aluminum reduction electrodes made of or coated with particular mixed-metal oxide materials. Yamada et al teach that the oxide electrodes or oxide-coated electrodes (e.g. oxide-coated carbon electrodes) resist oxidation when immersed in molten salts. Yamada et al teach directly depositing solid oxide coatings by flame spraying, plasma spraying and electroplating (column 7, lines 14-16), and report depositing oxide coatings using plasma spraying of semi-molten oxide granules (see, for example, column 11, lines 5-11). Yamada et al also teach two-step deposition of solid oxide coatings by first depositing (e.g. by dipping, spraying, thermal decomposition, etc.) a precursor coating comprising a metal and subsequently sintering the precursor coating to convert the precursor coating to a solid oxide coating (see column 7, lines 17-28), and report using a two-step process in which solid metal coatings were first deposited by electroplating and were then converted to oxides by oxidative sintering (see, for example, column 9, lines 11-21).

Neither of the methods taught by Yamada et al for forming solid oxide coatings involves direct formation of oxides from metal compounds, and neither of the methods taught by Yamada et al suggests the direct aerosol pyrolysis method of forming specialized fine powders taught by the present invention. Even one skilled in the art would not have arrived at the present invention by combining the solid coatings deposition methods taught by Yamada et al with the powder formation method taught by Douglas et al. For example, neither Yamada et al's first method of making gallium oxide coatings by plasma spraying using gallium oxide granules, nor Yamada et al's second method of, say, electroplating a Ga precursor coating and then oxidizing the metallic precursor coating to form an oxide coating would likely be combined with the Douglas et al method of making oxide particles directly from reactant solutions via aerosol pyrolysis to arrive at the direct powder processes taught by the present invention.

The new art disclosed by the present invention is patentably distinct from Yamada et al in light of Douglas et al and would not be obvious to one skilled in the art. Accordingly, applicants respectfully submit that the claims are patentable over the cited art and should be allowed.

Claims 30-32 and 36 were rejected under 35 U.S.C. 102(e) as anticipated by or, in the alternative under 35 U.S.C. 103(a) as obvious over Asada et al (US 5,964,918). Claims 31 and 32 have been canceled, and no corollary replacement claims have been submitted. Claims 30 and 36 have been replaced by new claims 54 and 57. The applicants respectfully submit that claims 54 and 57 are patentable over Asada et al.

Asada et al teach an aerosol pyrolysis method of preparing a metal powder in which the surface of the metal powder is in part coated with another material. The method of Asada et al involves mixing multiple metal-containing reactants together in a common solution, atomizing the solution into droplets, and heating the droplets to form powder in which the multiple metals automatically segregate into a particle comprising the "major metal" and a

surface deposit comprising the "metal or the like", e.g. a solution comprising Ag- and Ni-containing reactants reacted to form Ag powder with Ni oxide on the surface (see column 4, lines 59-64). All of the examples given by Asada et al involve Ag or Ag-Pd as the "major metal". While the present inventors believe that it is likely that the method of Asada et al works only for select noble metals (e.g. Ag and Pd) in which select secondary metals will segregate as oxides (e.g. Cu & Ni) or metals (e.g. Rh), Asada et al teach that the method is also applicable to major metals selected from the base metals including Cu and Al (see column 2, lines 39-41). For all "major metal" choices, Asada et al teach that the "metal or the like" not melt under conditions for forming the powder and that the "metal or the like" not hardly dissolve in solid solution form in the powder (see column 2, lines 53-58).

The applicants respectfully submit that the claims are limited to materials that do not meet the criteria of Asada et al, namely the metals groups defined in claim 54 do not meet the melting and/or dissolution criteria defined by Asada et al, and hence the present invention is not anticipated by or obvious over Asada et al.

The new art disclosed by the present invention is patentably distinct from Asada et al and would not be obvious to one skilled in the art. Accordingly, applicants respectfully submit that the claims are patentable over the cited art and should be allowed.

Conclusion

For all of the above reasons, applicants submit that the claims are now in proper form, and that the claims all define patentably over the prior art. Therefore they submit that this application is now in condition for allowance, which action they respectfully solicit.

Conditional Request for Constructive Assistance

Applicants have amended the claims of this application so that they are proper, definite, and define novel matter that is also unobvious. If, for any reason this application is not believed to be in full condition for allowance, applicant respectfully requests the constructive assistance and suggestions of the Examiner pursuant to M.P.E.P. §706.03(d) and § 707.07(j) in order that the undersigned can place this application in allowable condition as soon as possible and without the need for further proceedings.

The applicants can be reached by telephone at (805) 987-7258.

Very Respectfully,

 
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